

Synthesis of Large Areas of Highly Oriented, Very Long Silicon Nanowires**

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Silicon is one of the most important electronic materials. Its nanoscale forms, such as nanocrystals,^[1] porous silicon,^[2] quantum wells, and nanowires,^[3,4] have stimulated great interest among scientists because of their peculiar physical properties, such as light emission,^[2] field emission, and quantum confinement effects.^[5,6] The progress made in the synthesis of silicon nanostructures and nanowires in recent years has attracted considerable attention.^[7] Today, large quantities of silicon nanowires can be produced by the laser ablation of metal- or SiO₂-containing silicon targets,^[8] and a few properties, such as electric and thermal conductivity and optical properties, have also been studied.^[5,9,10] However, the experimental characterization and application of silicon nanowires, for example, the measurement of the elastic properties, the realization of efficient field emission of nanoscale silicon, and the fabrication of nanometer field effect transistors and planar displays, have been hampered so far because of the difficulty in growing oriented silicon nanowires. As a result, the production of highly oriented and very long silicon nanowires is a very important and challenging issue. In this communication, we report the successful synthesis of highly oriented, large-scale, and very long silicon nanowires on flat silicon substrates by thermal evaporation of silicon monoxide (SiO). The growth mechanism and optical properties of the oriented silicon nanowires are also discussed. To the best of our knowledge, the synthesis of oriented silicon nanowires has not yet been reported.

The equipment used for the present work is similar to that described previously.^[11] An alumina tube was mounted inside a tube furnace. The SiO powders (Goodfellow, 99.95 %) were placed near the middle of the high-temperature zone of the furnace. The polished silicon (100) substrates about 5 mm in width and 50 mm in length were ultrasonically cleaned in acetone, ethanol, and deionized water for 20 min each, dipped in 20 % HF for 20 min, and finally rinsed in deionized water for 20 min before they were placed abreast at one end of the alumina tube. The tube had previously been evacuated to a

base pressure of 10⁻² torr by a mechanical pump before the starting materials were heated. The carrier gas of argon mixed with 5 % H₂ admitted at the other end of the alumina tube flowed at 50 sccm (standard cubic centimeters per minute) at 400 torr. The temperature of the furnace was increased to 1300 °C at 6 °C/min and kept at this temperature for 7 h. The temperature of the silicon substrate surface where the oriented silicon nanowires grew was found to be approximately 930 °C, which differed from that at the center due to the temperature gradient within the tube.

The product was first directly examined by scanning electron microscopy (SEM, Philips XL 30 FEG). Microstructural characterization was carried out in a conventional Philips CM 20 transmission electron microscope (TEM) at 200 kV. The high-resolution transmission electron microscopy (HRTEM) study was performed in a Philips CM200 FEG transmission electron microscope, operated at 200 kV accelerating voltage at room temperature. The chemical compositions of the samples were determined by an energy dispersive X-ray (EDX) spectrometer attached to both the SEM and HRTEM instruments. Raman scattering spectra were measured with a Renishaw micro-Raman spectrometer at room temperature. Excitation was by means of the 514 nm line of an Ar⁺ laser, and the Raman signals were measured in a backscattering geometry with a spectral resolution of 1.0 cm⁻¹.

The deposited silicon nanowire product is light yellow in color. SEM images at different magnifications of a typical sample in Figures 1a, 1b, 1c, and 1d clearly show the large area of highly oriented nanowires on the surface of the silicon substrate. The low magnification SEM image (Fig. 1a) shows that the area of highly oriented silicon nanowires is about 2 mm × 3 mm and the lengths of individual nanowires are up to 1.5–2 mm. The thickness of the oriented nanowire product was about 10 μm, as estimated from the cross-sectional image (Fig. 1d) of the sample prepared by focused ion beam cutting. The highly oriented array of Si nanowires can also be observed from the cross-sectional image. The EDX results show that the nanowires are composed of silicon and oxygen. No metal was found in the sample. Such results are consistent with our previous theory that silicon nanowire growth is enhanced by silicon oxide instead of a metal particle catalyst.^[12] Because of local charging effects, the diameters observed from SEM images appear larger than the actual wire diameters. More information about the morphology of silicon nanowires is given by the following TEM characterization

Small pieces of oriented silicon nanowire samples were peeled off from a silicon substrate and mounted on a folding grid for TEM and HRTEM observations. Figure 2 shows the typical morphology of silicon nanowires. As reported previously, these nanowires show a better orientation than those synthesized by laser ablation.^[13] Silicon nanowires as observed by TEM are quite clean, with very few particles attached to their surfaces, and are relatively homogeneous. Analysis of a number of nanowires shows that the diameters of these silicon nanowires vary from 18 to 46 nm, and the mean value is about 30 nm. The selected-area electron dif-

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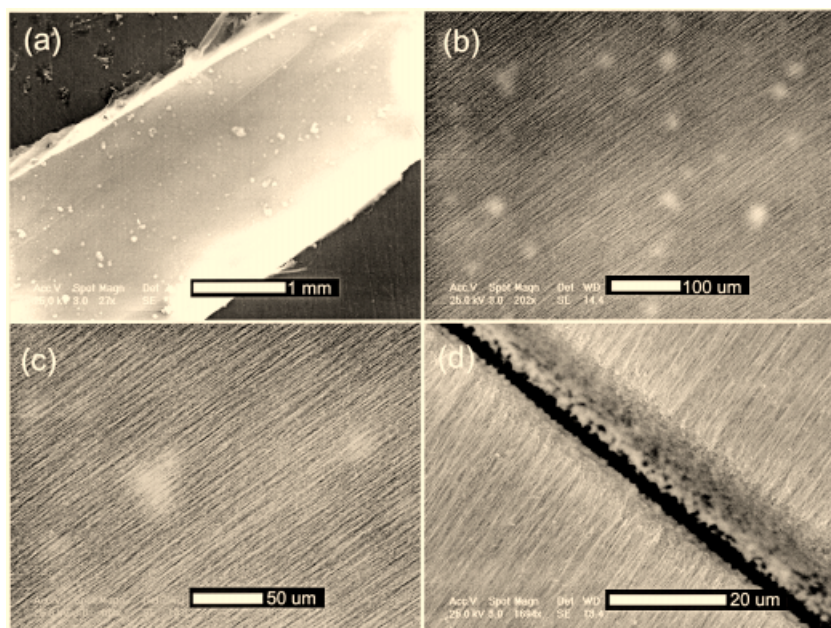


Fig. 1. a–c) SEM images of oriented silicon nanowires of different magnification. d) The cross section, cut by a focused ion beam.

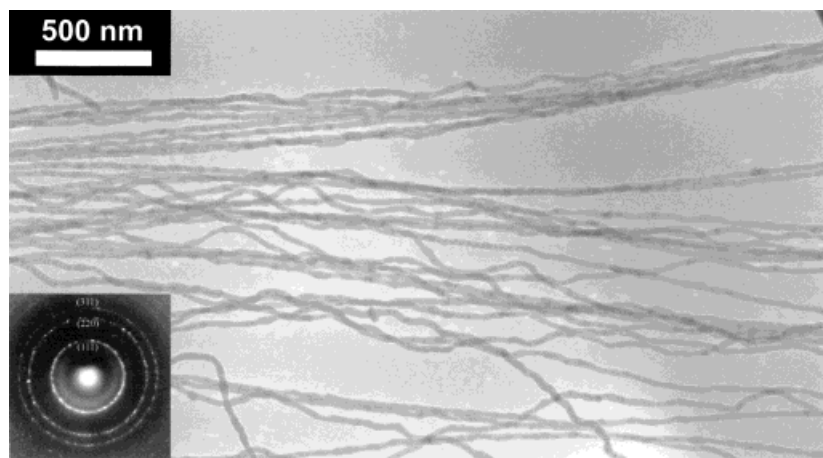


Fig. 2. TEM image of oriented silicon nanowires. The inset shows the SAED pattern.

fraction (SAED) pattern of the nanowires is shown in the inset in Figure 2.

The microstructure of silicon nanowires was further confirmed by HRTEM observations. Figure 3 gives a lattice image of a nanowire, in which the core–shell structure is clearly visible. The crystalline core is wrapped in an amorphous outer layer with an atomically sharp interface. The spacing between the parallel fringes of the crystalline core was measured to be 0.31 nm, that is equal to the spacing of the {111} planes of crystalline silicon. The composition of the amorphous shell consists of silicon and oxygen, as determined by EDX attached to the TEM, and the atomic ratio of oxygen to silicon is near 2:1. These results reveal that the amorphous shell consists of silicon oxide. HRTEM observations were carried out on many individual nanowires. The results showed that the diameters of the crystalline silicon core varied from 13 to

30 nm, and the mean value was about 20 nm. The thickness of the amorphous silicon oxide shell varied from 2 to 10 nm, and the mean value was about 5 nm. It is noteworthy that the cores of the silicon nanowires have a chain-like silicon nanocrystalline structure. These nanocrystals are connected by an ultrathin silicon oxide layer. This semiconductor–insulator–semiconductor nanostructure is similar to the silicon nanowires synthesized by electron beam annealing on amorphous silicon films, which showed the coulomb blockade effect that could be useful in a single-electron device.^[14] This suggests that the nanostructure of our silicon nanowires may also possess similar extraordinary electric effects worthy of further exploration.

The growth of the oriented silicon nanowires may be related to the flow of the carrier gas, because it was found that the orientation direction of the silicon nanowires is parallel to the direction of flow of the carrier gas in the alumina tube. An analysis of the growth of the oriented silicon nanowires is attempted below. First, the nucleation of silicon nanowires from silicon oxide (SiO_x) vapor started at the proper position of the substrates. Because there was a temperature gradient along the alumina tube, and the planes with the same temperature were perpendicular to the axial direction of the tube, only some particular positions with the appropriate temperature may be suitable for the nucleation of silicon nanowires.^[8,12] These positions should be located on a line of equal temperature on the substrate and will also be perpendicular to the flow direction of the carrier gas. Once initial nucleation is established, nanowire growth will tend to continue on the substrate.^[12] Secondly, the strength of the flow of the carrier gas will force the growing nanowires to grow in the direction of the flow. At the same time, overcrowding of the nanowires will limit the possibility of nanowire propagation in other directions.^[15] In addition, it was found that a smooth plane substrate is very helpful for oriented growth.

Raman scattering was carried out to further confirm the structure of the oriented silicon nanowires on a large scale. The results reveal a prominent Raman feature at $\sim 520 \text{ cm}^{-1}$ with a shoulder at $\sim 490 \text{ cm}^{-1}$ (Fig. 4). These may be attributed to the presence of a silicon oxide (SiO_x) shell, which has Raman scattering between 400 cm^{-1} and 550 cm^{-1} .^[16] In addition, the Raman peak at about 520 cm^{-1} becomes broadened in width and asymmetric in shape compared with the first-order optical phonon mode of single-crystal silicon. Such a feature

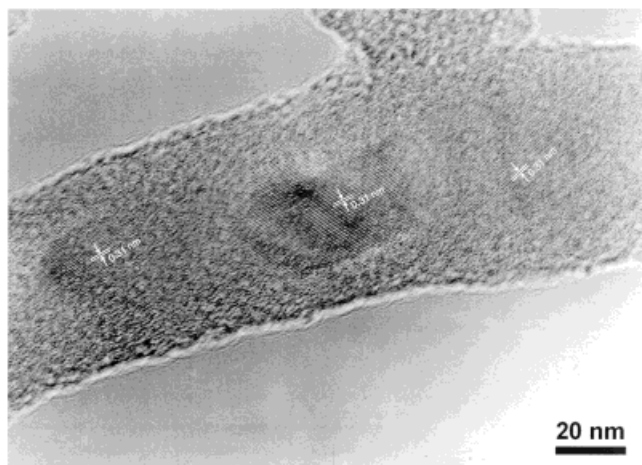


Fig. 3. HRTEM lattice image of an individual silicon nanowire. The crystalline semiconductor silicon in the core are separated by an ultrathin layer of amorphous silicon oxide.

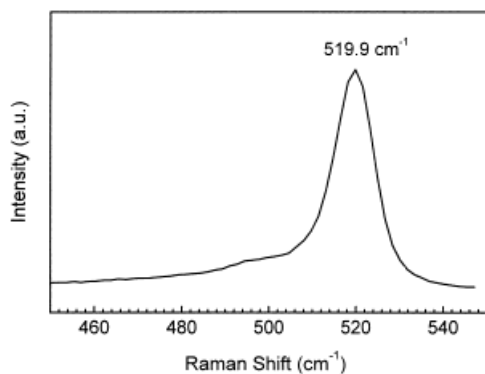


Fig. 4. Raman spectrum of oriented silicon nanowires.

could be due to the small size effect of Si nanocrystals and/or defects, as observed by HRTEM. For the characteristic Raman peak at 520 cm^{-1} , there is no obvious Raman frequency down-shift caused by the size confinement effect. This phenomenon is similar to that observed previously in randomly oriented silicon nanowires.^[16] It is known that the size confinement effect will not significantly affect the electron and phonon properties of crystals unless their size is less than the Bohr radius of silicon, which is less than 10 nm at room temperature. Because the average diameter of silicon nanowires or the average size of the chains in our sample is larger than 10 nm, it is understandable that no significant frequency down-shift caused by the size confinement effect was observed. However, there are always some silicon nanowires and nanoparticle chains of sizes less than the Bohr radius of silicon, which would give rise to a frequency down-shift in Raman scattering. This can also contribute to the broadening and asymmetry of the Raman peak of oriented silicon nanowires.

In summary, we have synthesized millimeter-area arrays of highly oriented, crystalline silicon nanowires of millimeter length by thermal evaporation of SiO powder. The growth area of the oriented silicon nanowires characterized by SEM

was about $2\text{ mm} \times 3\text{ mm}$. The thickness of the nanowire product was about $10\text{ }\mu\text{m}$. TEM revealed that oriented silicon nanowires consisted of crystalline silicon cores (20 nm in diameter, on average) covered by amorphous silicon oxide sheaths (5 nm thick on average). The silicon cores were semiconductor–insulator–semiconductor chain-like structures. Analysis of the optical properties as characterized by Raman scattering revealed that the Raman scattering peak at about 520 cm^{-1} was broadened and asymmetric with respect to the first-order optical phonon mode of single-crystalline silicon. The flowing carrier gas, the temperature gradient, and the planar substrate may be the main reasons for the formation of the oriented silicon nanowires. Our successful synthesis of large areas of highly oriented, very long silicon nanowires presents opportunities for further research on silicon nanostructure properties. Work on the properties of silicon nanowires related to their orientation is in progress.

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